PIEZO-ELECTRIC CONSTANTS OF CRYSTALS—GROUP-THEORETICAL TREATMENT

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ABSTRACT. The number of piezo-electric moduli and the relations between them have been obtained by using group-theoretical method. The results are in agreement with those given by Voigt.

INTRODUCTION

Some crystals develop an electric moment when they are subjected to mechanical stress. Such crystals are said to be piezo-electric. The components of stress t_{kz} or of strain r_{kz} are related to the components of electric moment p_i by relations of the type

$$p_i = q_{kzi}\, t_{kz} \text{ and } p_i = e_{kzi}\, r_{kz}$$

q_{kzi} and e_{kzi} are called piezo-electric moduli and piezo-electric constants respectively. There are 18 such constants and their number reduces to one for crystals of the cubic class and some crystals of the tetragonal and hexagonal classes. The relations for all the crystallographic point-groups were investigated by Voigt and a summary of this work in English is given by Wooster (1938). The derivation of these relations as usually given is rather complicated and it is therefore proposed to give here an easy method, based on the theory of groups, for obtaining the number of piezo-electric constants and their relations for all classes of crystal symmetry.

METHOD

The components of stress and of strain are second order tensors and therefore q_{kzi} and e_{kzi} are third order tensors. Second order tensors are given by nine coefficients which reduce to six in symmetric tensors on account of the relation $c_{rs} = c_{sr}$. The components of stress (also of strain) are given by six components t_{xx}, t_{yy}, t_{zz}, $t_{xy} = t_{yx}$, $t_{yz} = t_{zy}$, $t_{xz} = t_{zx}$. Under an operation R_ϕ consisting of a rotation through ϕ or a rotation reflection through ϕ, these coefficients transform as products of cartesian co-ordinates. The following relations show the transformation of cartesian co-ordinates and tensor components by a rotation about an axis of symmetry (z axis).

$$\left.\begin{array}{l} x \rightarrow x\cos\phi + y\sin\phi;\quad y \rightarrow -x\sin\phi + y\cos\phi; \text{ and} \\ z \rightarrow \pm z \text{ (negative sign refers to rotation reflection)} \end{array}\right\} \quad \ldots \quad (1)$$

$$\left.\begin{array}{l} R(t_{xx}) \rightarrow t_{xx}\cos^2\phi + t_{yy}\sin^2\phi + 2t_{xy}\sin\phi\cos\phi \\ R(t_{yy}) \rightarrow t_{xx}\sin^2\phi + t_{yy}\cos^2\phi - 2t_{xy}\sin\phi\cos\phi \\ R(t_{zz}) \rightarrow t_{zz} \\ R(t_{xy}) \rightarrow -t_{xx}\cos\phi\sin\phi + t_{yy}\cos\phi\sin\phi + t_{xy}(\cos^2\phi - \sin^2\phi) \\ \left.\begin{array}{l} R(t_{yz}) \rightarrow \pm t_{yz}\cos\phi \mp t_{xz}\sin\phi \\ R(t_{xz}) \rightarrow \pm t_{yz}\sin\phi \pm t_{xz}\cos\phi \end{array}\right\} \text{the lower sign refers to rotation-reflection.} \end{array}\right\} \quad \ldots \quad (2)$$

The piezo-electric moduli q_{kzi} (or the constants e_{kzi}) which connect the components of stress tensor (or the strain tensor) with the components of the electric moment vector will be 18 in number and may be written as

$$
\begin{array}{llllllllllll}
q_{xxx} & q_{yyx} & q_{zzx} & q_{yzx} & q_{xzx} & q_{xyx} & \text{or} & q_{11} & q_{21} & q_{31} & q_{41} & q_{51} & q_{61} \\
q_{xxy} & q_{yyy} & q_{zzy} & q_{yzy} & q_{xzy} & q_{xyy} & & q_{12} & q_{22} & q_{32} & q_{42} & q_{52} & q_{62} \\
q_{xxz} & q_{yyz} & q_{zzz} & q_{yzz} & q_{xzz} & q_{xyz} & & q_{13} & q_{23} & q_{33} & q_{43} & q_{53} & q_{63}
\end{array}
$$

if we write $xx \quad yy \quad zz \quad yz \quad xz \quad xy \;\;|\;\; x \quad y \quad z$

as $\;1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \;\;|\;\; 1 \quad 2 \quad 3$

The transformation matrix for various q_{kzi} can be easily written down with the help of the transformations (2) and (1)

$$
\left.
\begin{aligned}
R(q_{xxx}) &\longrightarrow q_{xxx}\cos^3\phi + q_{yyx}\cos\phi\sin^2\phi + 2q_{xyx}\sin\phi\cos^2\phi \\
&\quad + q_{xxy}\cos^2\phi\sin\phi + q_{yyy}\sin^3\phi + 2q_{xyy}\sin^2\phi\cos\phi \\
R(q_{yyx}) &\longrightarrow q_{xxx}\cos\phi\sin^2\phi + q_{yyx}\cos^3\phi - 2q_{xyx}\sin\phi\cos^2\phi \\
&\quad + q_{xxy}\sin^3\phi + q_{yyy}\cos^2\phi\sin\phi - 2q_{xyy}\sin^2\phi\cos\phi \\
R(q_{xyx}) &\longrightarrow - q_{xxx}\sin\phi\cos^2\phi + q_{yyx}\sin\phi\cos^2\phi + q_{xyx}\cos 2\phi\cos\phi \\
&\quad - q_{xxy}\sin^2\phi\cos\phi + q_{yyy}\sin^2\phi\cos\phi + q_{xyy}\cos 2\phi\sin\phi \\
R(q_{xxy}) &\longrightarrow - q_{xxx}\sin\phi\cos^2\phi - q_{yyx}\sin^3\phi - 2q_{xyx}\sin^2\phi\cos\phi \\
&\quad + q_{xxy}\cos^3\phi + q_{yyy}\sin^2\phi\cos\phi + q_{xyy}\, 2\cos^2\phi\sin\phi \\
R(q_{yyy}) &\longrightarrow - q_{xxx}\sin^3\phi - q_{yyx}\cos^2\phi\sin\phi + 2q_{xyx}\sin^2\phi\cos\phi \\
&\quad + q_{xxy}\cos\phi\sin^2\phi + q_{yyy}\cos^3\phi - q_{xyy}\, 2\sin\phi\cos^2\phi \\
R(q_{xyy}) &\longrightarrow q_{xxx}\sin^2\phi\cos\phi - q_{yyx}\sin^2\phi\cos\phi - q_{xyx}\cos 2\phi\sin\phi \\
&\quad - q_{xxy}\sin\phi\cos^2\phi + q_{yyy}\sin\phi\cos^2\phi + q_{xyy}\cos 2\phi\cos\phi
\end{aligned}
\right\} \quad \ldots \quad (3a)
$$

$$
\left.
\begin{aligned}
R(q_{yzx}) &\longrightarrow \pm q_{yzx}\cos^2\phi \pm q_{yzy}\cos\phi\sin\phi \mp q_{xzx}\sin\phi\cos\phi \mp q_{xzy}\sin^2\phi \\
R(q_{yzy}) &\longrightarrow \mp q_{yzx}\cos\phi\sin\phi \pm q_{yzy}\cos^2\phi \pm q_{xzx}\sin^2\phi \mp q_{xzy}\sin\phi\cos\phi \\
R(q_{xzx}) &\longrightarrow \pm q_{yzx}\cos\phi\sin\phi \pm q_{yzy}\sin^2\phi \pm q_{xzx}\cos^2\phi \pm q_{xzy}\sin\phi\cos\phi \\
R(q_{xzy}) &\longrightarrow \mp q_{yzx}\sin^2\phi \pm q_{yzy}\sin\phi\cos\phi \mp q_{xzx}\sin\phi\cos\phi \pm q_{xzy}\cos^2\phi
\end{aligned}
\right\} \quad \ldots \quad (3b)
$$

$$
\left.
\begin{aligned}
R(q_{xxz}) &\longrightarrow \pm q_{xxz}\cos^2\phi \pm q_{yyz}\sin^2\phi \pm q_{xyz}\, 2\sin\phi\cos\phi \\
R(q_{yyz}) &\longrightarrow \pm q_{xxz}\sin^2\phi \pm q_{yyz}\cos^2\phi \mp q_{xyz}\, 2\sin\phi\cos\phi \\
R(q_{xyz}) &\longrightarrow \mp q_{xxz}\sin\phi\cos\phi \pm q_{yyz}\sin\phi\cos\phi \pm q_{xyz}\cos 2\phi
\end{aligned}
\right\} \quad \ldots \quad (3c)
$$

$$
\left.
\begin{aligned}
R(q_{yzz}) &\longrightarrow q_{yzz}\cos\phi - q_{xzz}\sin\phi \\
R(q_{xzz}) &\longrightarrow q_{yzz}\sin\phi + q_{xzz}\cos\phi
\end{aligned}
\right\} \quad \ldots \quad (3d)
$$

$$
R(q_{zzz}) \longrightarrow \pm q_{zzz} \quad \ldots \quad (3e)
$$

$$
\left.
\begin{aligned}
R(q_{zzx}) &\longrightarrow q_{zzx}\cos\phi + q_{zzy}\sin\phi \\
R(q_{zzy}) &\longrightarrow - q_{zzx}\sin\phi + q_{zzy}\cos\phi
\end{aligned}
\right\} \quad \ldots \quad (3f)
$$

The character of the transformation matrix in (3) is given by $8\cos^3\phi \pm 8\cos^2\phi + 2\cos\phi$ ($+$ or $-$ sign to be taken according as the operation is a pure rotation or rotation-reflection).

The linear substitutions in (3) constitute a reducible representation of group G. The 18 mutually orthogonal and independent linear combinations in (3) can be divided into six sets (3*a*), (3*b*), (3*c*), (3*d*), (3*e*), (3*f*)—the members in each set transform among themselves for every operation of the group G. These will form the basis of a new and completely reducible representation of the group G and the character $R\phi$ in this representation is the same as before as the two are equivalent. The number of times n_i, a particular irreducible representation, repeats itself in the representation Γ of the new variables is given by (Wigner, 1931; Bhagavantam) $n_i = \frac{1}{N}\sum_j h_j \chi_i(R)\chi'(R)$ where $\chi_i(R)$ is the character of the irreducible representation, $\chi'(R)$ the character of Γ which is the same as that of the transformation matrix (3), h_j the number of elements in the j^{th} class of the point-group and N the order of the group. Since we want to know the number of combinations that remain invariant for all operations of group G we find n_i corresponding to the totally symmetric irreducible representation. Hence

$$\chi_i(R) = 1 \text{ and } n_i = \frac{1}{N}\sum h_j \chi'(R) \qquad \dots \quad (4)$$

where $\chi'(R) = 8 \cos^3\phi \pm 8 \cos^2\phi + 2 \cos \phi$, (the lower negative sign to be taken for rotation-reflection axes). This result gives the number of piezo-electric moduli for any given point-group as these moduli remain invariant for all operations of the group.

For the totally symmetric irreducible representation $R(q_{xyz}) = q_{xyz}$ and so we get 18 equations from (3*a*), (3*b*), etc., which enable us to find the relations between the various piezo-electric moduli. This gives yet another method of finding the number of piezo-electric moduli for any point-group. The vanishing piezo-coefficients for various symmetry operations are given below.

(1) z-axis as the axis of two-fold symmetry.

$$q_{xxx} = q_{xxy} = q_{yyx} = q_{yyy} = q_{zzx} = q_{zzy} = q_{yzz} = q_{xzz} = q_{xyx} = q_{xyy} = 0$$

These relations can be obtained from (3) by putting $\phi = \pi$ or directly. A symmetry about z-axis implies that for every point x, y, z there is another $-x$, $-y$, z. As the tensor components transform as products of cartesian co-ordinates $R(q_{xxx}) \longrightarrow -q_{xxx}$ but as $R(q_{xxx}) \longrightarrow q_{xxx}$ for the totally symmetric representation $q_{xxx} = -q_{xxx} = 0$.

(2) x-axis as the axis of two-fold symmetry

$$q_{xxy} = q_{xxz} = q_{yyy} = q_{yyz} = q_{zzy} = q_{zzz} = q_{yzy} = q_{yzz} = q_{xzx} = q_{xyx} = 0$$

(3) y-axis as the axis of two-fold symmetry

$$q_{xxx} = q_{xxz} = q_{yyx} = q_{yyz} = q_{zzx} = q_{zzz} = q_{yzy} = q_{xzx} = q_{xzz} = q_{xyy} = 0$$

(4) σ_z (plane perpendicular to z-axis) as plane of symmetry. A reflection in a plane is equivalent to a rotation reflection of 360°. Also the symmetry signifies that for every point x, y, z there is a point x, y, $-z$. Therefore by putting $\phi = 2\pi$ in (3) or directly as above

$$q_{xxz} = q_{yyz} = q_{zzz} = q_{yzx} = q_{yzy} = q_{xzx} = q_{xzy} = q_{xyz} = 0$$

(5) σ_y (plane perpendicular to y-axis) as plane of symmetry

$$q_{xxy} = q_{yyy} = q_{zzy} = q_{yzx} = q_{yzz} = q_{xzy} = q_{xyx} = q_{xyz} = 0$$

(6) σ_x as plane of symmetry

$$q_{xxx} = q_{yyx} = q_{zzx} = q_{yzx} = q_{xzy} = q_{xzz} = q_{xyy} = q_{xyz} = 0$$

(7) z-axis as the four-fold axis of rotation (C_4) and of rotation reflection (S_4) Substituting $\phi = \pi/2$ in (3) we get from (3*a*)

$$q_{xxy} = q_{yyx},\ q_{xxx} = q_{yyy},\ q_{xyx} = q_{xyy}$$
$$q_{xxy} = -q_{yyx},\ q_{xxx} = -q_{yyy},\ q_{xyx} = -q_{xyy}$$

$\therefore$ $q_{xxy} = q_{yyx} = 0$, $q_{xxx} = q_{yyy} = 0$, $q_{xyx} = q_{xyy} = 0$. Also from (3*b*) and (3*f*) $q_{yzz} = q_{xzz} = 0$, $q_{zzx} = q_{zzy} = 0$. From (3*b*) and (3*c*),

$q_{yzx} = \mp q_{xzy}$, $q_{yzy} = \pm q_{xzx}$, $q_{yyz} = \pm q_{xxz}$, $q_{xyz} = \mp q_{xyz}$, $q_{zzz} = \pm q_{zzz}$

TABLE I

System	Point group	Symmetry elements	No. of piezo-electric coeff.	Non-vanishing piezo-electric coefficients and their inter-relations
Tri-clinic	C_1	E	18	All coefficients
	C_i	E, i	0	
Mono-clinic	C_s	E, σ_z	10	$q_{11}, q_{12}, q_{21}, q_{22}, q_{31}, q_{32}, q_{43}, q_{53}, q_{61}, q_{62}$
	C_2	E, C_2^z	8	$q_{13}, q_{23}, q_{33}, q_{41}, q_{42}, q_{51}, q_{52}, q_{63}$
	C_{2h}	E, C_2^z, i, σ_z	0	
Ortho-rhombic	C_{2v}	E, C_{2z}, σ_x, σ_y	5	$q_{13}, q_{23}, q_{33}, q_{42}, q_{51}$
	D_2	E, C_{2z}, C_{2x}, C_{2y}	3	q_{41}, q_{52}, q_{63}
	D_{2h}	E, C_{2z}, C_{2x}, C_{2y}, i, σ_z, σ_x, σ_y	0	
Tetragonal	C_4	E, 2 C_{4z}, C_{2z}	4	$q_{13}=q_{23}, q_{33}, q_{41}=-q_{52}, q_{42}=q_{51}$
	S_4	E 2S_{4z}, C_{2z}	4	$q_{13}=-q_{23}, q_{41}=q_{52}, q_{42}=-q_{51}, q_{63}$
	C_{4h}	E, 2C_4^z, C_2^z, i, 2S_{4z}, σ_z	0	
	C_{4v}	E, 2C_{4z}, C_{2z}, 2σ_v, 2σ_v' (σ_x, σ_y)	3	$q_{13}=q_{23}, q_{33}, q_{42}=q_{51}$
	D_{2d}	E, C_2^z, C_2', C_2'', σ_v, 2S_4^z, σ_v'	2	$q_{13}=-q_{23}, q_{42}=-q_{51}$
	D_4	E, 2C_4^z, C_2^z, 2C_2, 2C_2' (C_2^x, C_2^y)	1	$q_{41}=-q_{52}$
	D_{4h}	E, 2C_4, C_2^z, 2C_2, 2C_2', i 2S_4, σ_z, 2σ_v, 2σ'_v	0	
Hexagonal	C_3	E, 2C_{3z}	6	$q_{11}=-q_{21}=-q_{62}$, $q_{22}=-q_{12}=-q_{61}$, $q_{13}=q_{23}$, q_{33}, $q_{41}=-q_{52}$, $q_{42}=q_{51}$
	S_6	E, 2C_{3z} i, 2S_6^z	0	
	C_{3v}	E, 2C_3^z, 3σ_v (σ_x or σ_y)	4	$q_{22}=-q_{12}=-q_{61}$, q_{33}, $q_{13}=q_{23}$, $q_{42}={}_{51}$ for σ_x ; $q_{11}=-q_{21}=-q_{62}$, q_{33}, $q_{13}=q_{23}$, $q_{42}=q_{51}$ for σ_y
	D_3	E, 2C_3^z, 3C_2 (C_2^x or C_2^y)	2	$q_{11}=-q_{21}=-q_{62}$, $q_{41}=-q_{52}$ for C_2^x, $q_{22}=-q_{12}=-q_{61}$, $q_{41}=-q_{52}$ for C_2^y
	D_{3d}	E, 2C_3, 3C_2, i, 2S_6, 3σ_v	0	
	C_{3h}	E, 2C_3^z, σ_z, 2S_3^z	2	$q_{11}=-q_{21}=-q_{62}$, $q_{22}=-q_{12}=-q_{61}$
	C_6	E, 2C_6^z, 2C_3^z, C_2^z	4	$q_{13}=q_{23}$; q_{33}, $q_{41}=-q_{52}$, $q_{42}=q_{51}$
	C_{6h}	E, 2C_6^z, 2C_3, C_2, i, 2S_6 2C_3, σ_z	0	
	D_{3h}	E, 2C_3^z, 3C_2, σ^z, 2S_3, 3σ_v [3σ'_v	1	$q_{11}=-q_{21}=-q_{62}$ for C_2^x and $q_{22}=-q_{12}=-q_{61}$ for C_2^y
	C_{6v}	E, 2C_6^z, 2C_3^z, C_2^z, 3σ_v,	3	$q_{13}=q_{23}$, q_{33}, $q_{42}=q_{51}$
	D_6	E, 2C_6^z, 2C_3^z, C_2^z, 3C_2, 3C_2'	1	$q_{41}=-q_{52}$
	D_{6h}	E, 2C_6, 2C_3, C_2, 3C_2, 3C_2', i, 2S_3, 2S_6, σ_z, 3σ_v, 3σ'_v	0	
Cubic	T	E, 3C_2 (C_2^x, C''_2, C_2^z), 8C_3	1	$q_{41}=q_{52}=q_{63}$
	T_h	E, 3C_2, 8C_3, i, 3σ, 8S_6	0	
	T_d	E, 3C_2, 8C_3, 6σ, 6S_4	1	$q_{41}=q_{52}=q_{63}$
	O	E, 8C_3, 3C_2, 6C_2, 6C_4	0	
	O_h	E, 8C_3, 3C_2, 6C_2, 6C_4 i, 8S_6, 3σ, 6σ, 6S_4	0	

the upper sign refers to pure rotation and the lower to rotation reflection. Thus for the C_4 axis $q_{xyz}=0$, but not for S_4 axis.

(8) z-axis an axis of more than two-fold symmetry ($C\phi$). From (3*a*) we have

$$q_{xxx}+q_{yyx}=\cos\phi\,(q_{xxx}+q_{yyx})+\sin\phi\,(q_{xxy}+q_{yyy})$$
$$q_{xxy}+q_{yyy}=-\sin\phi\,(q_{xxx}+q_{yyx})+\cos\phi\,(q_{xxy}+q_{yyy})$$
$$q_{xxx}+q_{xyy}=\cos\phi\,(q_{xxx}+q_{xyy})+\sin\phi\,(q_{xyx}+q_{yyy})$$
$$q_{xyx}+q_{yyy}=-\sin\phi\,(q_{xxx}+q_{xyy})+\cos\phi\,(q_{xyx}+q_{yyy})$$
$$\therefore\; q_{xxx}+q_{yyx}=0,\; q_{xxy}+q_{yyy}=0;\; q_{xxx}+q_{xyy}=0,\; q_{xyx}+q_{yyy}=0$$
$$\text{or } q_{xxx}=-q_{yyx}=-q_{xyy};\; q_{yyy}=-q_{xxy}=-q_{xyx}$$

from (3*d*) and (3*f*) $q_{zzx}=q_{zzy}=0;\; q_{yzz}=q_{xzz}=0$

from (3*c*) $q_{xxz}-q_{yyz}=\cos 2\phi\,(q_{xxz}-q_{yyz})+2q_{xyz}\sin 2\phi$
$$2q_{xyz}=-\sin 2\phi\,(q_{xxz}-q_{yyz})+2q_{xyz}\cos 2\phi$$
$$\therefore\; q_{xxz}-q_{yyz}=0;\; q_{xyz}=0$$

from (3*b*) $q_{yzx}+q_{xzy}=\cos 2\phi\,(q_{yzx}+q_{xzy})+\sin 2\phi\,(q_{yzy}-q_{xzx})$
$$q_{yzy}-q_{xzx}=-\sin 2\phi\,(q_{yzx}+q_{xzy})+\cos 2\phi\,(q_{yzy}-q_{xzx})$$
$$\therefore\; q_{yzx}+q_{xzy}=0,\; q_{yzy}-q_{xzx}=0$$

RESULTS

We are thus led to Table I for various point-groups. The second column gives the point-group (Schonfleiss notation), the third column the symmetry elements, the fourth the number of piezo-cofficients with the help of formula (4), and the last the relation between the coefficients or the non-vanishing coefficients with the help of the relations (1 to 8) found above.

It is seen that the piezo-electric effect does not exist in crystals having a centre of symmetry, and in cubic crystals belonging to point-group O having no centre of symmetry. The results in every case agree with those given in Wooster's book.

REFERENCES

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